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Mechanical Properties at the Protected Lithium Interface

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U.S. DEPARTMENT OF ENERGY

Overview

- Timeline
  - January 1, 2015 to May 31, 2019 Percent complete 100%
- Technical barriers
  - ***Li metal batteries - path to higher energy density, lower cost***
  - ***A solid-state Li battery – path to longer cycle life and safety***
    - ***When Li, and other materials, are used efficiently***
    - ***When premature and sudden failure processes are inhibited***
    - ***When practical, scalable fabrication is implemented***
    - Energy density (500-700 Wh/kg)
    - Cycle life, 3000 to 5000 deep discharge cycles
    - Safety
- Budget *This project is jointly funded by DOE and TARDEC.*

  $610K DOE

  $540K TARDEC

- Partners and collaborators

Michigan Tech Create the Future

Michigan Engineering University of Michigan

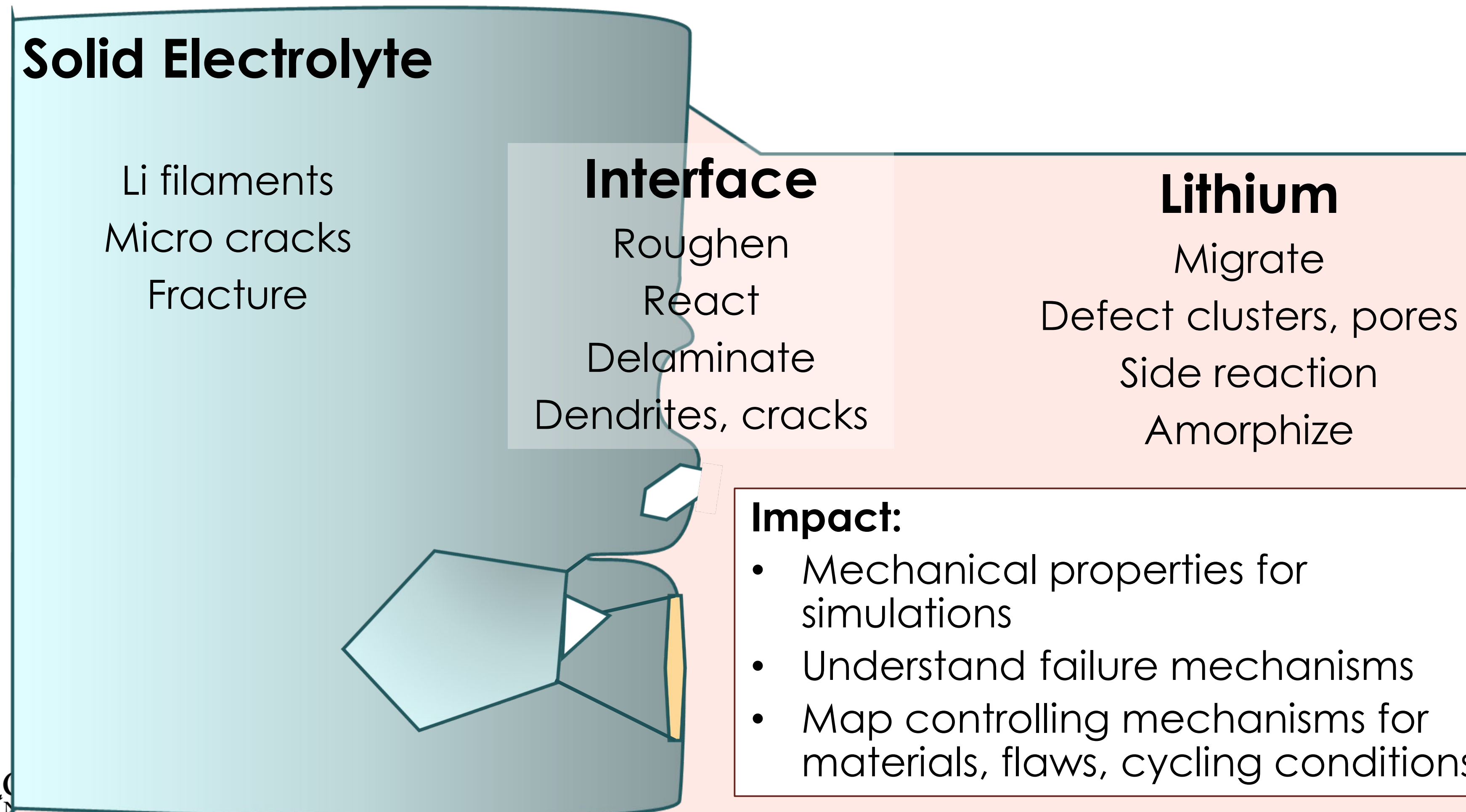
Oak Ridge National Laboratory

Nanomechanics, Inc.

OHARA Ohara Corporation

Relevance: Why probe the mechanical properties of the Li-solid electrolyte interface?

- Mechanical & (electro)chemical properties → all important for stability
- Interface and bulk must maintain continuity and good contact
- Both phases, and interface, may evolve/degrade with cycling.



Impact:
- Mechanical properties for simulations
- Understand failure mechanisms
- Map controlling mechanisms for materials, flaws, cycling conditions

Approach: probe buried interface–
mechanical tests give insight of Li-electrolyte interface

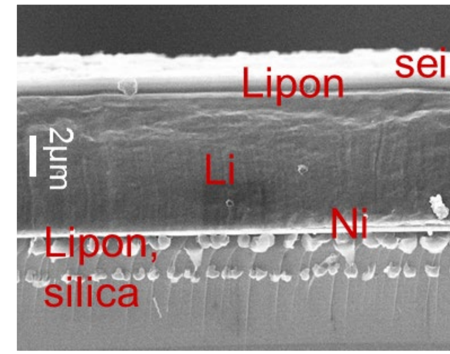
~mm → ~µm

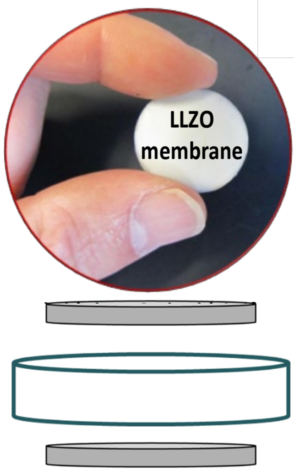
Li foil or
molten Li on
clean/polished
surface

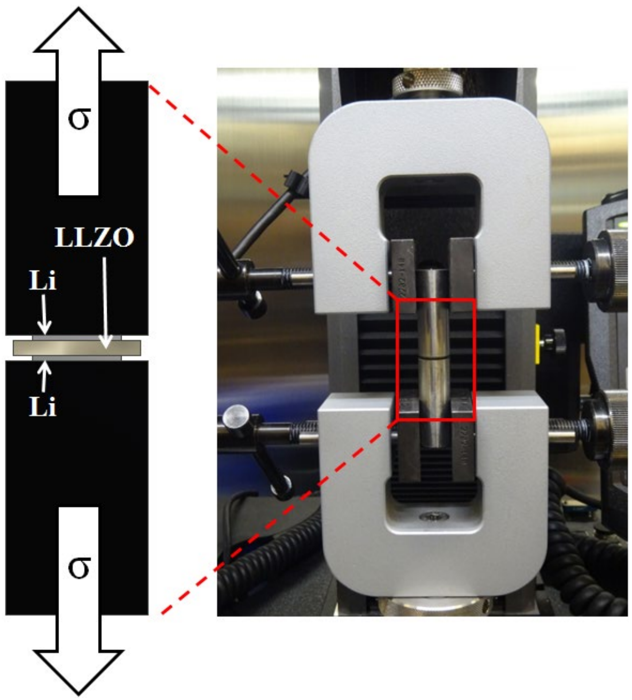
Test:
Li metal & LLZO, LATP, Lipon
Sample fabrication/conditioning
Before/after/during cycling

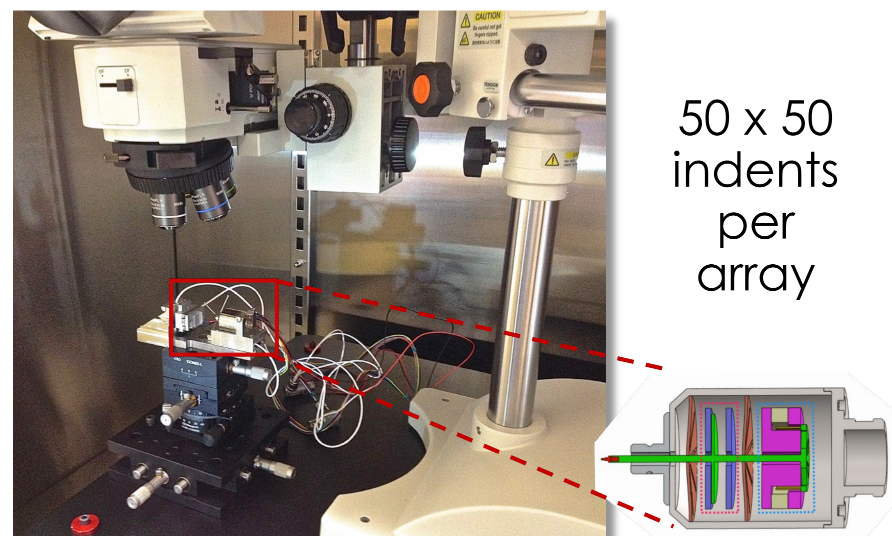
Tools in Ar atmosphere

Vapor
grow Li on
clean surface





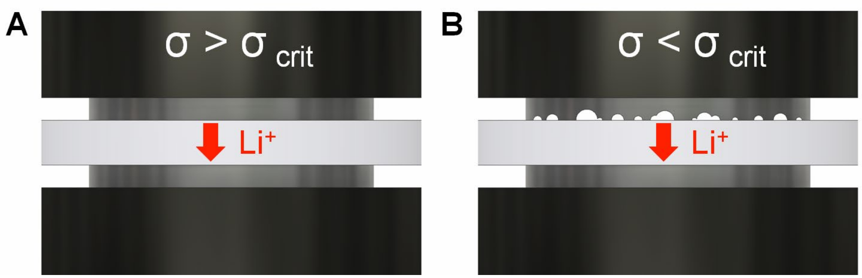




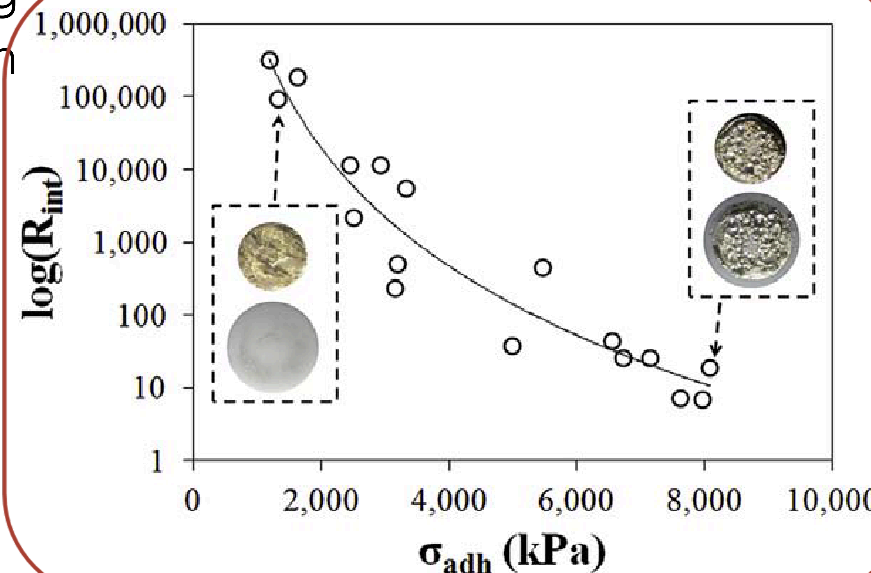
50 x 50
indents
per
array

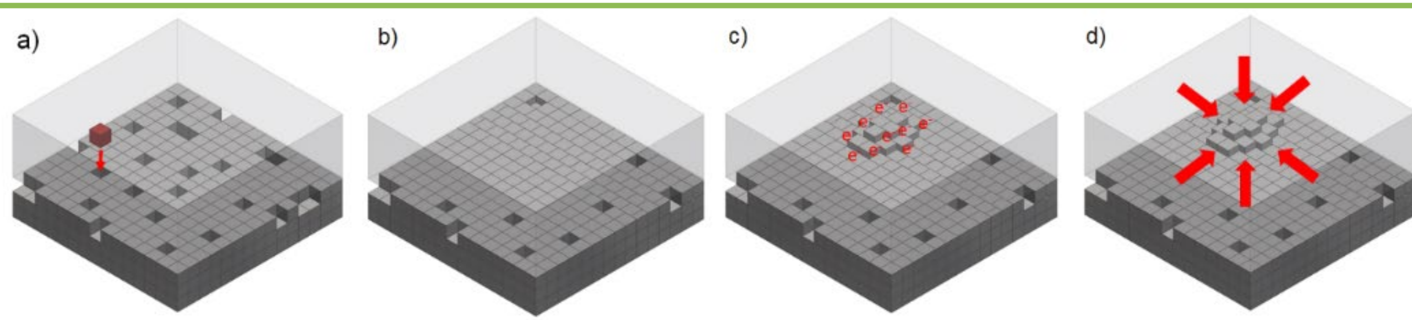
Lithium adheres well to clean solid electrolyte surface, but high currents may be trouble

- Strong adhesion – low ASR
- Flux imbalance on plating – hot spots
- Stack pressure – offset rapid Li stripping
- Map critical conditions for degradation



2MPa critical pressure for $0.4 mA/cm^2$





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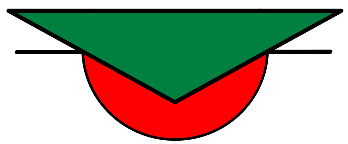
M. Wang, et.al. J Power S (2018); J.Electrochem. Acta, *in press*.; submitted

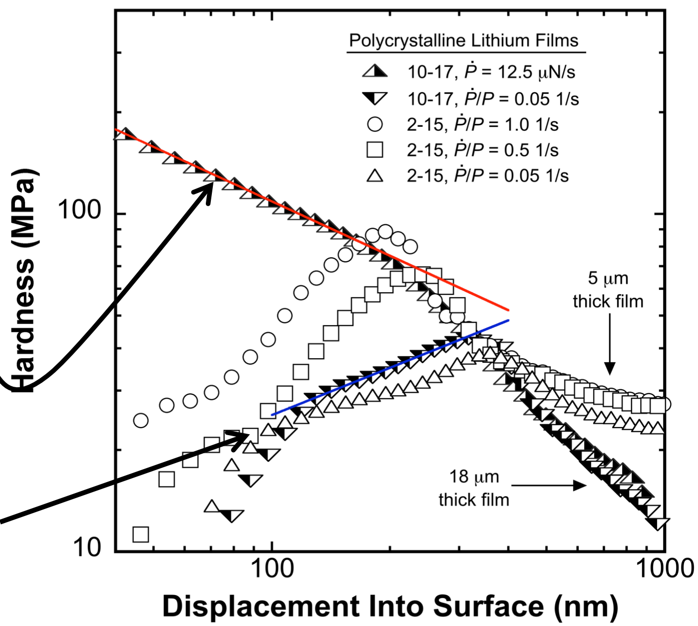
Small volumes of lithium can support ***high*** pressure



zone of hydrostatic compression

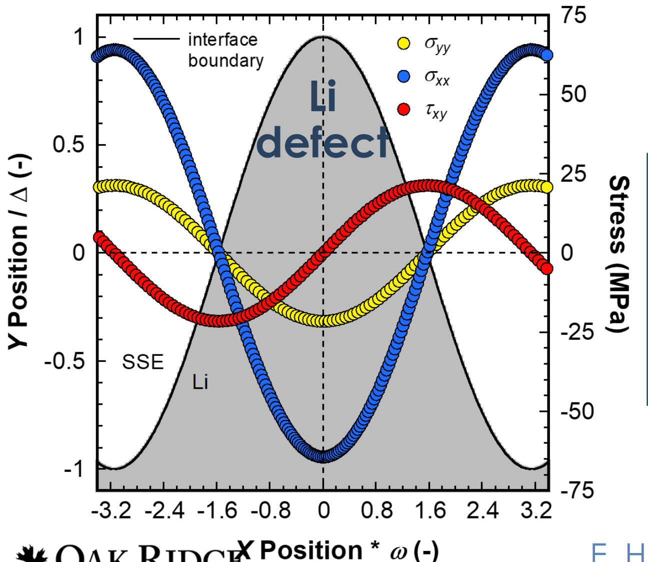
Harper-Dorn (non-conservative dislocation motion)

Nabarro-Herring (volume diffusion)



- Yield stress typical of bulk Li is ~0.5MPa.
- Dislocation mechanisms (Frank-Reed)need stress and room to operate

E. Herbert, et.al, J. Mat. Res. (2018)

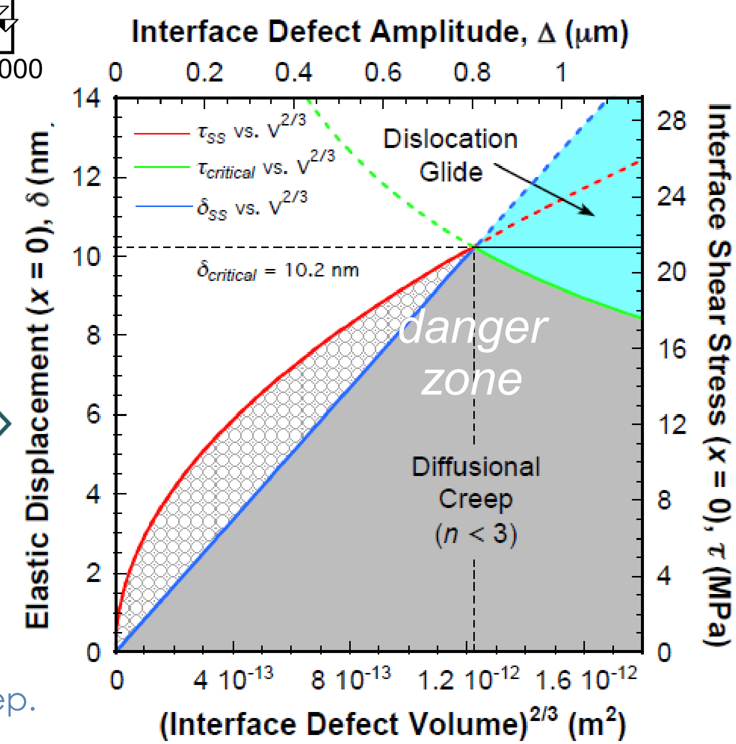


Prediction for:

Defect with A/λ=2*π*

E = 9 GPa

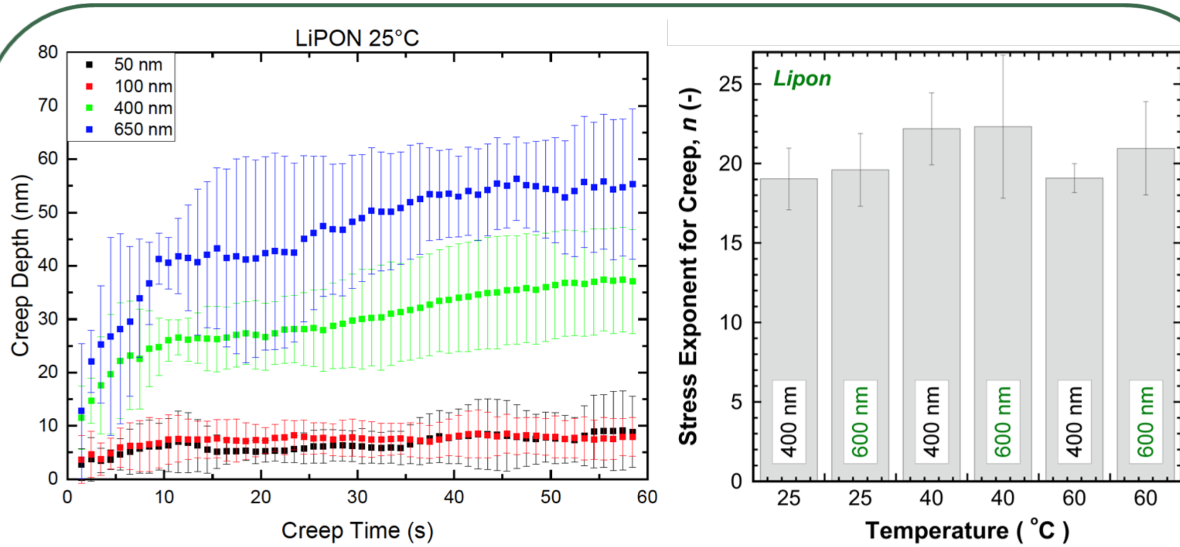
i = 1 mA/cm^2



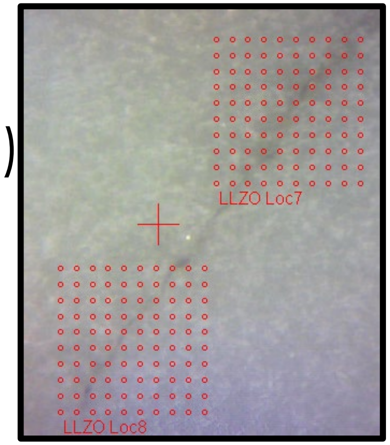
E. Herbert, et.al, manuscript in prep.

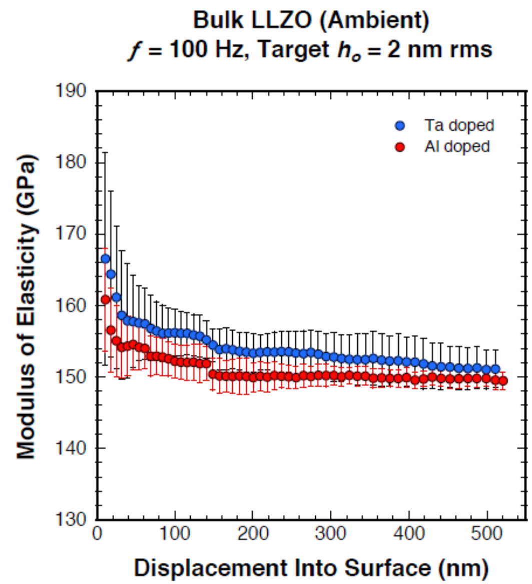
Mechanical and defect properties of the solid electrolyte also reveal surprises

- Electrolytes - high elastic modulus, no weak flaws
  - Ceramic > glass-ceramic > glassy films(155-77GPa)
    - 150-155 for doped LLZO, validating DFT theory
  - Damaged area not weakened
- Unexpected creep found for glassy electrolytes
  - High stress exponent consistent with PO_4 units



Herbert, unpublished. Creep of glassy Lipon at constant load (left). The stress exponent (right) for the power law strain rate dependence.





S. Yu, … D. J. Siegel, Chem. Mater., 2016.

Proposed Future Work

- Challenges, Risks and Mitigation
  - Move closer to relevant samples:
    - Full cells, efficient Li use, good current density, long cycling.
  - Separate: Li plating / stripping, defect formation / relaxation
- Future work - Map key processes operable for range of conditions.
  - Validate and extrapolate by simulation

Examples of factors contributing to Li cycling stability

Architecture of cell • Maximum Li anode thickness • Stack pressure • Overlap areas - current density	Nature of solid electrolyte • Mechanical properties • Uniformity of mass transfer • Flatness, flaws of interface • Thickness
Duty cycle (history) • Li plating versus stripping • % of Li removed each cycle • Timing of rests • Nature of the cathode	Nature of the Li metal • Purity, dissolved and particulates • Grain size, texture • Length scale • Temperature

Summary

- Relevance What happens at Li – solid electrolyte interface determines the cycle life and failure processes.

- Approach Determine the mechanical properties of the solid electrolyte, thin lithium anode, and their buried interface. Mechanical tests can provide a real-time measure of the lithium and electrolyte response to cycling.

- Accomplishments Correlated:
  - Critical stack loading to current density
  - Interface R and adhesion strength
  - Li hardness, length scale, dislocation processes
  - Creep properties of glassy electrolyte

- Future work Focus on physical/mechanical properties of bulk materials and interface. Map how these determine Li stability for particular cells and cycling.